

The product stream includes a trimer, which trimer is produced according to the invention in a continuous or batch fashion.

The process may include a process for trimerisation of α -olefins wherein α -olefins include all hydrocarbon compounds with terminal double bonds. This definition includes ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene and the like.

The process may include a process for trimerisation of α -olefins to yield trimeric α -olefin products selectively.

The ethylene may be contacted with the catalyst system at a pressure of 100 kPa (1 barg), preferably greater than 1000 kPa (10 barg), more preferably greater than 3000 kPa (30 barg).

By heteroatomic is meant a ligand that contains at least two heteroatoms, which may be the same or different, and may be independently selected from any one of a group which comprises phosphorus, arsenic, antimony, sulphur, nitrogen, oxygen, bismuth and selenium. The heteroatomic ligand may be described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and R is independently selected from any homo or hetero hydrocarbyl group and n and m are determined by the respective valence and oxidation state of A and C.

More specifically the ligand may be described by the following general formula: $(R^1)(R^2)A-B-C(R^3)(R^4)$, where A and C are independently phosphorus, arsenic, antimony, nitrogen and bismuth and B is a linking group between A and C. A and/or C may be a potential donor site for coordination with the transition metal.

An electron donor is defined as that entity that donates electrons used in chemical, including dative covalent, bond formation.

A and/or C may be independently oxidised by S, Se, N or O.

It is most preferred that all of R^1 , R^2 , R^3 and R^4 may be aromatic or hetero aromatic and each of R^1 , R^2 , R^3 and R^4 should be substituted on at least one of the atoms adjacent to the atom bound to A or C by a non-electron donating group. It is also preferred that R^1 , R^2 , R^3 and R^4 be aromatic or hetero aromatic and each of R^1 , R^2 , R^3 and R^4 be substituted on at least one of the atoms adjacent to the atom bound to A or C by a non-polar group.

Any of the groups R^1 , R^2 , R^3 and R^4 may independently be linked to one or more of each other or to the linking group B to form a cyclic structure together with A and C, A and B or B and C.

The ligand may also contain multiple $(R)_nA-B-C(R)_m$ units. Not limiting examples of such ligands include dendrimeric ligands as well as ligands where the individual units are coupled either *via* one or more of the R groups or *via* the linking group B. More specific, but not limiting, examples of such ligands may include 1,2-di-(N(P(*o*-ethylphenyl)₂)₂)-benzene, 1,4-di-(N(P(*o*-ethylphenyl)₂)₂)-benzene, N(CH₂CH₂N(P(*o*-ethylphenyl)₂)₂)₃ and 1,4-di-(P(*o*-ethylphenyl)N(methyl)P(*o*-ethylphenyl)₂)-benzene.

The ligands can be prepared using procedures known to one skilled in the art and procedures disclosed in published literature. Examples of these ligands are: (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂, (*o*-isopropylphenyl)₂PN(methyl)P(*o*-isopropylphenyl)₂, (*o*-methylphenyl)₂PN(methyl)P(*o*-methylphenyl)₂, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)(phenyl), (*o*-ethylphenyl)₂PN(isopropyl)P(*o*-ethylphenyl)₂, (*o*-isopropylphenyl)₂PN(isopropyl)P(*o*-isopropylphenyl)₂, (*o*-methylphenyl)₂PN(isopropyl)P(*o*-methylphenyl)₂, (*o*-*t*-butylphenyl)₂PN(methyl)P(*o*-*t*-butylphenyl)₂, (*o*-*t*-butylphenyl)₂PN(isopropyl)P(*o*-*t*-butylphenyl)₂, (*o*-ethylphenyl)₂PN(pentyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(phenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(*p*-methoxyphenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(benzyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(1-cyclohexylethyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(2-methylcyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(cyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(allyl)P(*o*-ethylphenyl)₂, (3-ethyl-2-thiophenyl)₂PN(methyl)P(3-ethyl-2-thiophenyl)₂, (2-ethyl-3-thiophenyl)₂PN(methyl)P(2-ethyl-3-thiophenyl)₂ and (2-ethyl-4-pyridyl)₂PN(methyl)P(2-ethyl-4-pyridyl)₂.

The catalyst system, in accordance with the invention, or its individual components, may also be immobilised by supporting it on a support material, for example, silica, alumina, MgCl_2 , zirconia or mixtures thereof, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene). The catalyst can be formed *in situ* in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. In some cases, the support material can also act as or as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with a chromium-based ethylene trimerisation catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, **109**, 177-179. In some cases, the support can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLATM (a product from Grace Davison).

The reaction products, or in other words olefin oligomers, as described herein, may be prepared with the disclosed catalyst system by homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic as well as aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, cyclohexane, 1-hexene, ionic liquids and the like.

The process may be carried out at pressures from atmospheric to 50000 kPa (500 barg). Ethylene pressures in the range of 1000–10000 kPa (10-100 barg) are preferred. Particularly preferred pressures range from above 3000–5000 kPa (30-50 barg). Catalyst activities and/or selectivities improve with pressures above 100 kPa (1 barg).

temperature. The reaction was left stirring overnight and the solvent removed *in vacuo*. The crude product was found to be a mixture of (Br:Cl)-phosphines. This crude product was not isolated and all was used in the next step

Example 1c) : Preparation of (o-Ethylphenyl)₂PN(methyl)P(o-Ethylphenyl)₂

The Bis(o-ethylphenyl) phosphorus chloride (30 mmol from the crude reaction mixture) was added to a solution of methylamine (2.0 M sol. in THF, 6.5 ml, 13.0 mmol) in DCM (80 ml) and triethylamine (15 ml) at 0 °C. The reaction was stirred for 30 min after which the ice bath was removed. After stirring for a total of 14 hrs the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallisation in 85 % yield. ³¹P {H} NMR: 57.45 ppm (s)

Example 2: Ethylene trimerisation reaction using CrCl₃.(Tetrahydrofuran)₃, (o-ethylphenyl)₂PN(methyl)P(o-ethylphenyl)₂ and MAO

A solution of 33.7 mg of (o-ethylphenyl)₂PN(methyl)P(o-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 12.4 mg CrCl₃.(Tetrahydrofuran)₃ (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was allowed to gradually increase to 4500 kPa (45 barg) over a period of 15 minutes. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.4358 g of

polyethylene. The GC analyses indicated that the reaction mixture contained 68.91 g oligomers. The product distribution of this example is summarised in Table 1.

Example 3: Ethylene trimerisation reaction using $\text{CrCl}_3 \cdot (\text{Tetrahydrofuran})_3$, $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})_2$ and MAO

A solution of 22.5 mg of $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})_2$ (0.044 mmol) in 5 ml of toluene was added to a solution of 8.3 mg $\text{CrCl}_3 \cdot (\text{Tetrahydrofuran})_3$ (0.022 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 6.6 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5033 g of polyethylene. The GC analyses indicated that the reaction mixture contained 102.60 g oligomers. The product distribution of this example is summarised in Table 1.

Example 4: Ethylene trimerisation reaction using Cr(III) acetylacetonate, $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})_2$ and MAO

A solution of 33.7 mg of $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})_2$ (0.066 mmol) in 5 ml of toluene was added to a solution of 11.5 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor

temperature was maintained at 55°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.3665g of polyethylene. The GC analyses indicated that the reaction mixture contained 41.72 g oligomers. The product distribution of this example is summarised in Table 1.

Example 5: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO

A solution of 33.7 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 11.5 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.95 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 2.03 g of polyethylene. The GC analyses indicated that the reaction mixture contained 15.63 g oligomers. The product distribution of this example is summarised in Table 1.

Example 6: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO

A solution of 11.1 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.022 mmol) in 5 ml of toluene was added to a solution of 4 mg Cr(III) acetylacetonate (0.012 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 3.3 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.1 g of polyethylene. The GC analyses indicated that the reaction mixture contained 32.16 g oligomers. The product distribution of this example is summarised in Table 1.

Example 7: Ethylene trimerisation reaction using Cr(III) (2-ethylhexanoate), (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO

A solution of 33.7 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 22.7 mg Cr(III) (2-ethylhexanoate) (70 mass % in mineral oil, 0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 55°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas

entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.8270 g of polyethylene. The GC analyses indicated that the reaction mixture contained 86.57 g oligomers. The product distribution of this example is summarised in Table 1.

Example 8: Ethylene trimerisation reaction using Cr(III) (2-ethylhexanoate), (o-methylphenyl)₂PN(methyl)P(o-methylphenyl)₂ and MAO

A solution of 30.1 mg of (o-methylphenyl)₂PN(methyl)P(o-methylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 22.7 mg Cr(III) (2-ethylhexanoate) (70 mass % in mineral oil, 0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 55°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 60°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5009g of polyethylene. The GC analyses indicated that the reaction mixture contained 70.18 g oligomers. The product distribution of this example is summarised in Table 1.

Example 9: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-methylphenyl)₂PN(Me)P(*o*-methylphenyl)₂ and MAO

A solution of 30.1 mg of (*o*-methylphenyl)₂PN(Me)P(*o*-methylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 11.5 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 13 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.9579g of polyethylene. The GC analyses indicated that the reaction mixture contained 70.89 g oligomers. The product distribution of this example is summarised in Table 1.

Example 10: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-isopropylphenyl)₂PN(methyl)P(*o*-isopropylphenyl)₂ and MAO

A solution of 37.5 mg of (*o*-isopropylphenyl)₂PN(Me)P(*o*-isopropylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 11.5 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 13 minutes by discontinuing the

ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.3748g of polyethylene. The GC analyses indicated that the reaction mixture contained 56.30 g oligomers. The product distribution of this example is summarised in Table 1.

Example 11: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MMAO-3A

A solution of 6.9 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.0135 mmol) in 10 ml of toluene was added to a solution of 3.5 mg Cr(acac)₃ (0.01 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (77ml) and MMAO-3A (modified methylaluminoxane, Akzo Nobel, 3.0 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 2.931 g of polyethylene. The GC analyses indicated that the reaction mixture contained 48.29 g oligomers. The product distribution of this example is summarised in Table 1.

Example 12: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and EAO/TMA

A solution of 33.7 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acac)₃ (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml), EAO (ethylaluminumoxane, 33 mmol) and TMA (trimethylaluminium, 0.80ml, 8.3 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 46 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.0g of polyethylene. The GC analyses indicated that the reaction mixture contained 45.27 g oligomers. The product distribution of this example is summarised in Table 1.

Example 13: Ethylene trimerisation reaction using Cr(octanoate)₃, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO

A solution of 16.0 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.031 mmol) in 5 ml of toluene was added to a solution of 14.5 mg Cr(octanoate)₃ (0.021 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminumoxane, 4.0 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction

was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.331 g of polyethylene. The GC analyses indicated that the reaction mixture contained 18.56 g oligomers. The product distribution of this example is summarised in Table 1.

Example 14: Ethylene trimerisation reaction using Cr(III) acetylacetonate, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ and MAO in cyclohexane as solvent

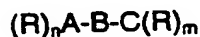
A solution of 33.9 mg of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂ (0.066 mmol) in 5 ml of cyclohexane was added to a solution of 11.7 mg Cr(III) acetylacetonate (0.033 mmol) in 15 ml cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of cyclohexane (71ml) and MAO methylaluminoxane, 9.9 mmol) in toluene (9 ml) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 3.2g of polyethylene. The GC analyses indicated that the reaction mixture contained 37.53 g oligomers. The product distribution of this example is summarised in Table 1.

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Claims

1. A process for trimerisation of olefins which process includes the step of contacting an olefinic feedstream with a catalyst system at a pressure above 100 kPa (1 barg) which catalyst system includes the combination of

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



where

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen;

B is a linking group between A and C and is selected to exclude $(CH_2)_xY(CH_2)_y$, where Y is $-P(R^6)-$, $-N(R^6)-$, $-As(R^6)-$, $-Sb(R^6)-$ or $-S-$ and x and y are individually 1-15 and wherein R^6 is selected from the group consisting of hydrogen, a halogen, a nitro group, or a hydrocarbyl group and a substituted hydrocarbyl group;

the R-groups are the same or different, and each R is independently selected from any homo or hetero hydrocarbyl group, and without any electron donating substituents on R; and

n and m is each determined by the respective valence and oxidation state of A and C.

2. The process as claimed in claim 1, wherein the ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth, and nitrogen; B is as defined in claim 1; and R^1 , R^2 , R^3 and R^4 are each independently selected from the group consisting of a hydrocarbyl group, a substituted hydrocarbyl group a heterohydrocarbyl group and a substituted hetero hydrocarbyl group.

3. The process as claimed in claim 2, wherein R^1 , R^2 , R^3 and R^4 are independently selected from aromatic, including hetero aromatic, groups of which two or more of R^1 , R^2 , R^3 and R^4 are substituted on the atom adjacent to the atom bound to A or C.

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4. The process as claimed in claim 2, wherein all of R^1 , R^2 , R^3 and R^4 have non-electron donating substituents on the atom adjacent to the atom bound to A and C.
5. The process as claimed in any one of claims 1 to 4, wherein any non-electron donating substituent is non-polar.
6. The process as claimed in any one of claims 1 to 5, wherein ethylene is contacted with the catalyst system at a pressure of more than 10 barg.
7. The process as claimed in any one of claims 1 to 6, wherein B is selected from the group consisting of an organic linking group containing a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl group; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
8. The process as claimed in any one of claims 1 to 7, wherein B is a single atom linking spacer.
9. The process as claimed in any one of claims 1 to 8, wherein B is $-N(R^5)-$, wherein R^5 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and an aryl group substituted with any of these substituents.
10. The process as claimed in any one of claims 1 to 9, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
11. The process as claimed in any one of claims 1 to 9, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.

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12. The process as claimed in claim 2, wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of methyl, ethyl, ethylenyl, propyl, propenyl, propynyl, butyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, benzyl, phenyl, tolyl, xylol, *o*-methylphenyl, *o*-ethylphenyl, *o*-isopropylphenyl, *o*-*t*-butylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl and dimethylhydrazyl group.

13. The process as claimed in Claim 12, wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of *o*-methylphenyl, *o*-ethylphenyl, *o*-isopropylphenyl, *o*-*t*-butylphenyl, phenyl, tolyl, biphenyl, and naphthyl group.

14. The process as claimed in any one of claims 1 to 9 and 11 to 13 wherein the ligand is selected from the any one of a group consisting of (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂, (*o*-isopropylphenyl)₂PN(methyl)P(*o*-isopropylphenyl)₂, (*o*-methylphenyl)₂PN(methyl)P(*o*-methylphenyl)₂, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)(phenyl), (*o*-ethylphenyl)₂PN(isopropyl)P(*o*-ethylphenyl)₂, (*o*-isopropylphenyl)₂PN(isopropyl)P(*o*-isopropylphenyl)₂, (*o*-methylphenyl)₂PN(isopropyl)P(*o*-methylphenyl)₂, (*o*-*t*-butylphenyl)₂PN(methyl)P(*o*-*t*-butylphenyl)₂, (*o*-*t*-butylphenyl)₂PN(isopropyl)P(*o*-*t*-butylphenyl)₂, (*o*-ethylphenyl)₂PN(pentyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(phenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(*p*-methoxyphenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(benzyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(1-cyclohexylethyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(2-methylcyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(cyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(allyl)P(*o*-ethylphenyl)₂, (3-ethyl-2-thiopheneyl)₂PN(methyl)P(3-ethyl-2-thiopheneyl)₂, (2-ethyl-3-thiopheneyl)₂PN(methyl)P(2-ethyl-3-thiopheneyl)₂ and (2-ethyl-4-pyridyl)₂PN(methyl)P(2-ethyl-4-pyridyl)₂.

15. The process as claimed in any one of the claims 1 to 14, wherein the catalyst system is prepared by combining in any order the heteroatomic ligand with the transition metal compound and an activator.

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16. The process as claimed in claim 15, which includes the step of generating a heteroatomic coordination complex *in situ* from the transition metal compound and the heteroatomic ligand.
17. The process as claimed in any one of claims 1 to 16, which process includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and the transition metal compound, to a reaction mixture containing an activator.
18. The process as claimed in any one of the claims 1 to 17, wherein the transition metal in the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
19. The process as claimed in claim 18, wherein the transition metal is chromium.
20. The process as claimed in claim 15 or claim 16, wherein the transition metal compound is selected from an inorganic or organic salt, a co-ordination or organometallic complex.
21. The process as claimed in claim 20, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.
22. The process as claimed in claim 21, wherein the transition metal compound is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
23. The process as claimed in any one of claims 16 to 22, wherein the transition metal compound and heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.
24. The process as claimed in claim 23, wherein the transition metal compound and heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.1:1 to 10:1.

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25. The process as claimed in either one of claims 15 or 16, wherein the activator is selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyllithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.
26. The process as claimed in claim 25, wherein the activator is an alkylaluminoxane.
27. The process as claimed in claim 26, wherein the alkylaluminoxane, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO) or mixtures thereof.
28. The process as claimed in claim 26 or claim 27, wherein the transition metal from the transition metal compound and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.
29. The process as claimed in claim 28, wherein the transition metal compound and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 1000:1.
30. The process as claimed in claim 29, wherein the transition metal compound and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 300:1.
31. The process as claimed in any one of claims 26 to 30, which includes the step of adding to the catalyst system a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of alkylaluminoxane.
32. The process as claimed in any one of claims 1 to 31, which includes the step of mixing the components of the catalyst system at any temperature between -20°C and 250°C in the presence of an olefin.

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33. The process as claimed in claim 32, wherein the temperature range is between 20°C and 100°C

34. The process as claimed in any one of the claims 1 to 33, wherein the process is carried out at temperatures in the range of 0-120 °C.

35. The process as claimed in any one of the claims 1 to 33, wherein the process is carried out at a temperature range from 25-100°C.

36. The process as claimed in any one of the claims 1 to 35, which includes the step of adding a polymerisation catalyst so that co-polymerisation of the olefin and trimerisation product occurs simultaneously leading to the incorporation of the trimerisation products into a copolymer.

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